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Dow Report AR-3S-63

MASS SPECTRAL STUDIES BEHIND SHOCK WAVES

II. THE THERMAL DECOMPOSITION OF HYDRAZINE

by

R. W. Diesen

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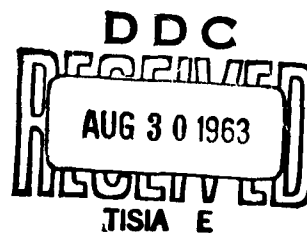
The Dow Chemical Company

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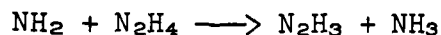
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At the lowest temperatures the reaction:



appears to become important.

From the experimental concentrations a value of

$$k_3 = 2.5 \times 10^{13} \text{ cc./mole-sec. (2000}^\circ\text{K.)}$$

is obtained. An order of magnitude estimate gives

$$k_4 \sim 10^{14} \text{ cc./mole-sec. (2000}^\circ\text{K.)}$$

## INTRODUCTION

A previous paper<sup>1</sup> described the use of a shock tube coupled to a time-of-flight mass spectrometer for the determination of the kinetics of a simple system, the thermal dissociation of molecular chlorine. The present investigation is of a more complicated system: the high temperature decomposition of hydrazine. In addition to obtaining information on the reaction of nitrogen-hydrogen radicals at high temperatures, a study of the decomposition of hydrazine should provide an indication of the general applicability of the approach and an indirect assessment of experimental apparatus whereby the relatively stable products of decomposition ( $\text{N}_2$ ,  $\text{H}_2$ ,  $\text{NH}_3$ ) can be calibrated under conditions of reaction.

In contrast to the heterogeneous decomposition<sup>2</sup>, the homogeneous thermal decomposition of hydrazine has not received extensive investigation. Szwarc<sup>3</sup>, using a toluene carrier technique, determined the homogeneous rate of the primary step and deduced a bond dissociation energy of 60 kcal./mole for the N-N bond in hydrazine.

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<sup>1</sup>R. W. Diesen and W. J. Felmlee, "Part I: Thermal Dissociation of Chlorine," (Dow Report AR-2S-63).

<sup>2</sup>See for example: J. C. Elgin and H. S. Taylor, J. Am. Chem. Soc., 51, 2059 (1929); P. J. Askey, *ibid.*, 52, 970 (1930); T. J. Hanratty, J. N. Pattison, J. W. Clegg, and A. W. Lemmon, Jr., Ind. Eng. Chem., 43, 1113 (1951); H. W. Lucien, J. Chem. Eng. Data, 6, 584 (1961).

<sup>3</sup>M. Szwarc, Proc. Roy. Soc. (London), A198, 267 (1949).

A number of investigations<sup>4</sup> have been made using self-sustaining flame techniques with reaction rate data deduced from the flame velocity. Moberley<sup>5</sup> and Palmer and Knox<sup>6</sup>, using a single pulse "chemical" shock tube, and Jost and Mickel<sup>7</sup>, using time resolved spectroscopy, have determined rate constants for the decomposition of hydrazine and found, as in the flame investigations, an apparent activation energy substantially less than the bond dissociation energy. The low activation energies observed were explained in terms of a chain mechanism.

From the onset of this study, it was estimated that, for the high temperatures and moderate pressures of the present investigation, the decomposition of hydrazine would be at or near the second order region, since the fall off to the second order region increases in pressure as the temperature is increased<sup>8</sup>. On this basis, it is possible, at sufficiently low partial pressures in an inert gas, to slow down significantly the rate of bimolecular processes (but not the primary step) and thereby to "magnify" the relative concentration of intermediates to a measurable level. The experimental results are consistent with this premise and a relatively high concentration of the amino radical was observed.

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<sup>4</sup>R. C. Murray and A. R. Hall, Trans. Faraday Soc., 47, 743 (1951); G. K. Adams and G. W. Stocks, "Fourth Symposium (International) on Combustion," Williams and Wilkins, Baltimore, 1953, p. 239; A. R. Hall and H. G. Wolfhard, Trans. Faraday Soc., 52, 1520 (1956); M. Gilbert, Combustion and Flame, 2, 149 (1958); P. Gray and J. C. Lee, "Seventh Symposium (International) on Combustion," Butterworths Publication, Ltd., London, 1959, p.61; A. C. Antoine, "Eighth Symposium (International) on Combustion," Williams and Wilkins, Baltimore, 1961, p. 1057.

<sup>5</sup>W. H. Moberly, J. Phys. Chem., 66, 366 (1962).

<sup>6</sup>H. B. Palmer, private communication; B. E. Knox, Ph.D. Thesis, Pennsylvania State University, 1963.

<sup>7</sup>W. Jost, "Investigation of Gaseous Detonations and Shock Wave Experiments with Hydrazine," University of Göttingen, Report No. ARL 62-330, April, 1962; K. W. Mickel, private communication.

<sup>8</sup>N. B. Slater, Trans. Roy. Soc. (London), A246, 57 (1953).

## EXPERIMENTAL

The apparatus is essentially that described in Part I with a slight modification of the ion source. The backing plate of the commercial ion source was removed and the electron beam assembly was realigned to put the electron beam closer to the exit of the sample nozzle. This was done to effectively increase the pressure of the sample being analyzed, and thus decrease the effective background due to scattering in the ion source. With this modification the electron beam is approximately 1 to 1.5 mm. from the sampling nozzle.

Olin Mathieson anhydrous hydrazine, 95%, was distilled and then center cut on the vacuum line by bulb to bulb transfer and analyzed mass spectrometrically to be better than 99% pure. Reaction mixtures containing between 0.5 and 1.0 mole percent hydrazine in argon and calibration mixtures containing 1.0% hydrogen, 0.5% nitrogen, 0.5% ammonia in argon were prepared with the aid of a gas burette and a Töpler pump. No internal pressure standard was added to these mixtures since the  $^{36}$  isotope (0.34%) of argon was in a convenient mass range and of a convenient intensity to coincide with the spectral intensities of interest.

The conditions prevailing behind the reflected shock wave were calculated as previously described<sup>1</sup> utilizing the experimentally determined shock velocity of the incident shock wave. For the reactant mixtures used, the enthalpy of reaction produces an insignificant change in the conditions behind the reflected shock wave, a necessary condition to maintain isothermal and isobaric conditions, and initial temperatures are reported. This introduces a maximum error of 40°K. which is within the anticipated accuracy of the production of these conditions behind the reflected shock wave. The experimental procedure is the same as described previously<sup>1</sup>.

The solubility of hydrazine in the stopcock grease of the gas handling system and the greased neoprene "O" ring at the end of the shock tube was sufficient to slowly decrease the hydrazine concentration in the argon mixture prior to execution of a run. This

observed solubility was compensated by adding a measured small amount of hydrazine to "season" the system, followed by a timed period of evacuation prior to the introduction of the reactant mixture and a timed period before a run. Some early runs were performed without using this procedure on samples containing 0.5% hydrazine with the resultant concentration varying between 0.1 and 0.5% depending on the sample handling history.

## RESULTS

The decomposition of hydrazine diluted in argon was studied over a temperature range of 1200° to 2500°K. The disappearance and appearance of the major species during decomposition were determined as a function of time, temperature and pressure. In addition, calibration under shock wave conditions was performed to check the material balance of the reaction during decomposition on an individual analysis basis.

A mass spectral bar graph of an experimental record is shown in Figure 1. The uninteresting peaks of the inert gas argon are excluded in this bar graph for simplification.

The first reaction spectrum is within 5 microseconds after the arrival of the shock wave and is essentially that of the starting material. The second spectrum, 25 microseconds later, shows a decrease in the hydrazine peaks, a small appearance of mass unit 2 (hydrogen) and 28 (nitrogen) and a large increase in mass unit 16. In the subsequent spectra, the 16 peak and hydrazine decrease while nitrogen, hydrogen and ammonia (major peak at 17) increase. This large abundance of mass unit 16 (and some 15) is taken as direct evidence for the  $\text{NH}_2$  radical.

The time dependence of the five major species observed (hydrazine, ammonia, nitrogen, hydrogen and the  $\text{NH}_2$  radical) is plotted for three different temperatures in Figures 2, 3, and 4. These plots are in terms of mole fractions with the mass spectral results converted



from intensities to concentrations. All of the species except the  $\text{NH}_2$  radical were calibrated (relative to argon) under reaction conditions<sup>9</sup> and the mass spectral sensitivity of the  $\text{NH}_2$  radical was assumed equal to that of  $\text{NH}_3$ <sup>10</sup>.

Although only three of the numerous runs are illustrated, they do show most of the general features of the experimental results and represent the central and temperature extremes for which calibration data were obtained.

The abundance of the amino radical (based on hydrazine) increases at the higher temperatures and at lower partial pressures of hydrazine. At temperatures below 1600° to 1700°K. the abundance of the amino radical is relatively small and is not detected experimentally.

The formation of the  $\text{NH}_2$  radical precedes in time the formation of ammonia, followed by nitrogen and hydrogen formation. In some runs, particularly at the higher temperatures, the first spectrum is obtained just after the onset of decomposition and the  $\text{NH}_2$  radical is the only observable species (in addition to hydrazine). From the observed concentration of the  $\text{NH}_2$  radical and a consideration of the detection limit of  $\text{NH}_3$ , an upper limit of the possible primary process going directly to  $\text{NH}_3$  and  $\text{NH}$  is less than 0.1 that going to  $\text{NH}_2$ . In the latter stages of decomposition, the measurement of the  $\text{NH}_2$  concentration becomes quite uncertain, not only because the concentration is small but also because the numerical value is obtained by the difference of two large numbers (subtraction of  $\text{NH}_3$  peaks).

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<sup>9</sup>The sensitivities of  $\text{N}_2\text{H}_4$ ,  $\text{NH}_3$ , and  $\text{N}_2$  (relative to argon) were found to be 10-30% greater under shock wave conditions than conventional type steady state calibration. On the other hand, the hydrogen sensitivity was found to decrease by approximately a factor of three. The reason for this is not completely understood except that part of the decrease appears to be defocusing due to the velocity vector and the space charge effects of the large amount of  $\text{Ar}^+$ .

<sup>10</sup>J. W. Otvos and D. P. Stevenson, J. Am. Chem. Soc., 78, 546 (1956).

The material balance during decomposition is within the experimental error of 10% of the total with the greatest uncertainty for hydrogen. The ratio of ammonia to nitrogen, a variable although significant number, decreases during the course of decomposition to the value of approximately two (slightly less at the higher temperatures and somewhat greater at the lower temperatures).

This changing ratio is primarily due to the formation of ammonia prior (in time) to nitrogen and indicates an additional intermediate between ammonia and nitrogen formation. In many runs the initial ratio is greater than 4, the stoichiometric limit. Although this intermediate has not been unequivocally identified, a few possibilities are suggested. The most likely intermediate appears to be NH at the higher temperatures and  $N_2H_3$  at the lowest temperatures.

The mass 15 residue may arise either from fragmentation of  $NH_2$  upon ionization or from NH and as will be seen from the Discussion is hard to distinguish kinetically. The maximum concentration of NH is approximately one-fourth the  $NH_2$  concentration<sup>11</sup>. At the higher  $NH_2$  concentrations, a small but reproducible residue at mass unit 29 is also observed, suggesting the presence of the  $N_2H$  radical. Direct evidence suggesting the existence of this radical has been obtained by Lavrovskaya et al.<sup>12</sup> from a study of the hot tube pyrolysis of pure hydrazine at 1000°K. by means of a charge exchange ionization mass spectrometer. However, the possible observation of this radical presents somewhat of a dilemma in terms of bond strengths<sup>13</sup>. A possible upper limit on the concentration of the  $N_2H$  radical is estimated to be 1/10 the  $NH_2$  concentration.

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<sup>11</sup>Sensitivity calculated from reference 10.

<sup>12</sup>G. K. Lavrovskaya, M. I. Markin and V. L. Talrose, Proc. All-Union Conf. Analysis of Organic Substances, Moscow (1961). [See V. L. Talrose, Pure and Appl. Chem., 5, 477 (1962)].

<sup>13</sup>From the heat of formation of gases hydrazine and H atoms, the reaction  $N_2H_4 = N_2 + 4H$  is endothermic by ~186 kcal./mole [JANAF Thermochemical Tables, The Dow Chemical Co., Dec. 31, (1960)]. Accepting a value of  $D(N_2H_3-H) \sim 76$  kcal./mole [S. N. Foner and R. L. Hudson, J. Chem. Phys., 29, 442 (1958)] and  $D(N_2H_2-H) \sim 54$  kcal./mole [S. N. Foner and R. L. Hudson, J. Chem. Phys., 28, 719 (1958)], then 56 kcal. is the sum of the last two bonds. In order for  $N_2H$  to be thermally stable enough to be even seen in our case,  $D(N_2-H) = 25$  to 30 kcal./mole leaving  $D(N_2H-H) = 31$  to 26 kcal./mole, a rather low value.

The presence of some hydrogen atoms<sup>14</sup> have been indicated but this is difficult to assess experimentally since the focusing of the time-of-flight mass spectrometer is very critical at the very low mass units. In a few runs at the higher temperatures, the mass spectrometer was favorably focused for the low masses (at the expense of the remainder of the spectrum) and mass unit one was observed but with considerable fluctuation. Because of the difficulties of detection of mass unit one, and of calibration of the relatively high mass discrimination, the concentration of hydrogen atoms can only crudely be estimated to be between one-twentieth and one-quarter the maximum amino radical concentration.

No evidence was found at the higher temperatures for the presence of the  $N_2H_3$  radical, a radical of known existence and importance in many nitrogen hydride reactions. At the lowest temperatures, small reproducible residues are observed at mass units 29, 30 and 31; however, there is considerable uncertainty in these residues (since they are obtained from the difference of two rather large numbers) and does not permit positive identification. At temperatures around 1200°K., where the rate is too slow to be measured from the disappearance of hydrazine, the ratio of  $NH_3$  to  $N_2$  is  $\sim 10$ . This value cannot be accounted for in terms of  $NH$ .

There is no evidence for nitrogen atoms either at the high or low temperatures with the mass residue of the small 14 peaks being statistically zero. The possible maximum upper limit for nitrogen atoms is less than one-tenth the  $NH_2$  concentrations. Blank runs with just ammonia in argon demonstrated that ammonia is thermally stable under the conditions of the present investigation.

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<sup>14</sup>A few crude experiments were performed with an excess of deuterium added to the hydrazine-argon mixtures with the result of HD formation presumably by atom exchange. A small amount ( $\sim 10$ -15%) of  $NH_2D$  was observed but was difficult to unscramble due to the limited accuracy of the peak intensities.  $NH_2D$  presumably arises from the reaction of  $NH_2$  with the excess deuterium (giving a source of deuterium atoms). No deuterium was detected in the hydrazine peaks.

# RATE OF DISAPPEARANCE OF HYDRAZINE

From the rate of disappearance of hydrazine, first order rate constants were determined. The log of the decrease of the hydrazine concentration versus time gives a reasonably straight line as seen in Figures 2, 3, and 4. Some runs were performed with as little as 0.1% hydrazine but with increased scatter of the points. Within this rather large uncertainty, first order dependence in hydrazine was observed. The observed rate constants are summarized in Table I. Although the total pressure could only be varied over a range of a factor of 4 to 8, the first order rate constants are approximately linear with pressure, systematically decreasing somewhat at the lower temperatures.

An Arrhenius plot at constant concentration of  $7 \pm 0.7 \times 10^{-4}$  mole/liter is shown in Figure 5. The effect of pressure on the first order rate constants along with the observation of a decrease of the Arrhenius activation energy with temperature supports the expectation that the reaction is in the fall off region at or near the second order limit.

At the second order limit, the observed activation energy,  $E_{ob}$ , is given in classical terms<sup>15</sup> of the Rice-Ramsperger-Kassel formulation by the relationship  $E_{ob} = E_0 - (s-1) RT$ , where  $E_0$  is the minimum energy for dissociation and  $s$  the effective number of internal degrees of freedom. The curvature of the solid line in Figure 5 is fit by a value of  $s \sim 12$ , a plausible although not necessarily significant value<sup>16</sup>.

<sup>15</sup>See R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," Cambridge University Press, New York, 1952, p. 522.

<sup>16</sup>The number of internal degrees of vibrational freedom is 12 ( $3N-6$ ), which at face value agrees with  $s \sim 12$ . However, a value of  $s \sim 12$  is embarrassingly high since IR shows [E. Catalano, R. H. Sanborn and J. W. Frazer, J. Chem. Phys., 38, 2265 (1963)] only 8 vibrational modes which have  $h\nu/kT$  less than or even of the order of unity. Consideration of experimental error and the possibility of some chain contribution at the lowest temperatures (see Discussion) narrow this difference considerably. Although the classical approximation is the best in the second order region, it is realized that this is not a good approximation [R. A. Marcus and O. K. Rice, J. Phys. and Colloid Chem., 55, 894 (1951) and B. S. Rabinovitch and R. W. Diesen, J. Chem. Phys., 30, 735 (1959) for example]. Also the completeness of fall off has not been well documented experimentally. For the purposes of the present paper these points are not considered further. However, it is hoped that a calculation of the fall off characteristics of hydrazine will be performed in the near future. (See also footnote 17).

The following non-chain mechanism is proposed to explain the experimental observation at the higher temperature (high  $\text{NH}_2$  concentration):

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The primary process is the rupture of the N-N bond in hydrazine to form  $\text{NH}_2$  radicals, which is the sole product observed during the initial phases of decomposition at the higher temperatures and, as discussed earlier, places an upper limit on  $k_{2b}$ ,  $k_{2b} \leq k_{2a}/10$ . The

pressure and temperature dependence of the disappearance of hydrazine indicates the decomposition is unimolecular, at or near the second order limit where collisional activation is the rate determining step.

The ability to study the reaction in the second order region and at high temperature is of special utility for the present investigation because the mechanism can be "forced" to reveal information concerning intermediate steps and, depending on the rate constants of the many potential reactions, can be manipulated to yield a relatively simple non-chain reaction sequence which facilitates the interpretation. For example, if it is assumed that reaction (1) is rate-controlling for the formation of  $\text{NH}_2$  and reaction (3) is the only reaction path, then at maximum  $\text{NH}_2$  concentration, the relative  $\text{NH}_2$  concentration is given by:

$$(\text{NH}_2)/(\text{N}_2\text{H}_4) = [k_1(\text{M})/k_3(\text{N}_2\text{H}_4)]^{1/2} \quad (10)$$

Alternatively, if  $\text{NH}_2$  reacts with another species  $x$ , then at maximum  $\text{NH}_2$  concentration:

$$(\text{NH}_2)/(\text{N}_2\text{H}_4) = 2k_1(\text{M})/k_x(\text{X}) \quad (11)$$

and for the case where  $\text{X} \equiv \text{N}_2\text{H}_4$ , a relationship similar to that in equation (10) is obtained except for the square root (and a factor of two). Since  $k_3(k_x)$  is likely to be essentially temperature independent, the relative  $\text{NH}_2$  concentration can be increased (to a measurable quantity) by increasing the temperature ( $k_1$ ) and decreasing the initial partial pressure of hydrazine,  $(\text{N}_2\text{H}_4)/(\text{M})$ . This is observed experimentally with a square root relationship correlating well with the data at the higher temperatures where the maximum  $\text{NH}_2$  concentration can be measured simultaneously with the hydrazine concentration.

On the basis of the proposed mechanism, the rate constant ( $k_3$ ) for the disproportionation of the  $\text{NH}_2$  radicals can be evaluated from equation (10). From the experimental rate data and the interpolated value of  $(\text{NH}_2)/(\text{N}_2\text{H}_4)$  at the maximum  $\text{NH}_2$  concentration, an average

value of  $k_3 = 2.5 \times 10^{13}$  cc./mole-sec. is obtained in the temperature range 1900° to 2400°K.<sup>17</sup>. It is estimated from error considerations and uncertainties in the mechanism that this value is correct within a factor of 2 to 3 in an absolute sense.

This value corresponds to a collision efficiency of one in ten if 3.3 Å is taken as the collision cross-section for NH<sub>2</sub>. In passing, if it is assumed the equivalent of recombination occurs on every fourth collision<sup>18</sup>, then a value of ~0.4 is obtained for the disproportionation-recombination ratio of the amino radical<sup>19</sup>.

The rather high collision efficiency for the reaction of amino radicals along with the experimental observation of a relatively high concentration (relative both to hydrazine and other intermediates) imparts a rather stringent requirement on the ensuing mechanism and, for the purposes of evaluation  $k_3$ , it is only necessary to show no major reaction of NH<sub>2</sub> other than reaction (3). At the maximum NH<sub>2</sub> concentration, any reaction involving NH<sub>2</sub> which competes equally with reaction (3) necessitates a comparable concentration or a rate constant in excess of  $2.5 \times 10^{13}$  cc./mole-sec.

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<sup>17</sup>The change in  $k$  over this temperature range is expected to be small. An estimate can be made for the temperature dependence of reaction (3), if it is assumed the value of  $2.2 \times 10^{12}$  cc./mole-sec. obtained by M. H. Hanes and E. I. Bair [(J. Chem. Phys., 38, 672 (1963))] for the recombination of NH<sub>2</sub> radicals (near ambient temperature) is actually that for disproportionation, an interpretation not in serious disagreement with their results since they measured the rate of disappearance of NH<sub>2</sub> which was found to be second order. Based on this assumption, an Arrhenius activation energy of 1.7 kcal./mole is obtained, being reduced to 1.0 kcal./mole when a  $T^{1/2}$  correction is made.

<sup>18</sup>Based on electron spin restriction.

<sup>19</sup>If these numbers are taken at face value, it can be argued on the basis of the numerical value of  $k_3$  and the upper limit of  $k_{2b}$  that the activated complex for disproportionation is different than for recombination (the back reaction of 2a is uneventful in our case since the reaction is in the second order region).

A probable important and efficient reaction in the mechanism is reaction (4), the equivalent of recombination of NH radicals. Lacking an alternative path, the highly excited  $N_2H_2^*$  would probably redissociate to reactants (i.e., in the second order region). However, the  $\sim 110$  kcal./mole of excitation<sup>20</sup> should be quite sufficient to overcome the activation energy required for the four center reaction (4b) which would be expected to be of the order of 40-50 kcal./mole<sup>21</sup>. Alternatively, the rupture of one or both of the hydrogen bonds would be endothermic by 56 or less kcal./mole<sup>13</sup>. These reactions should have energy barriers less than  $\sim 110$  kcal./mole required for the rupture of the newly formed nitrogen-nitrogen double bond (back reaction). The large exothermicity of (4b), and the possibly lower activation energy, suggest that the four-centered reaction would be predominant (however, some contribution of (4c) or (4d) cannot be excluded).

Reactions (5) and (6) are possible exothermic reaction of any  $N_2H$  or H formed. On the basis of the experimental upper limits on the concentration of  $N_2H$  and H, these reactions would make only a minor contribution unless the rate constants are much greater than  $10^{13}$  cc./mole-sec.<sup>22</sup>.

<sup>20</sup>S. N. Foner and R. L. Hudson, J. Chem. Phys., 28, 719 (1958).

<sup>21</sup>S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., N.Y. 1960, p. 290-299.

<sup>22</sup>A note of caution is in order on this point, particularly in reference to hydrogen atoms. (Thermal instability of  $N_2H$  would also give hydrogen atoms.) Although there is a good mass balance for hydrogen, there is also a considerable experimental uncertainty in the determination of H and  $H_2$  concentration. The limit of these uncertainties does not exclude the possibility of forming a significant amount of H atoms. This does not mean, however, that reactions (5), or (8), could be important since it is not necessary for the hydrogen atoms to react to an appreciable extent during the time of investigation. For example, if it is assumed at the maximum  $NH_2$  concentration, that all of the stoichiometrically possible hydrogen is really H atoms, the ratio  $H/NH_2$  is still less than unity. On the basis of  $k_5 = 10^{13}$  cc./mole-sec., this would be only a percentage contribution to the disappearance of  $NH_2$  radicals and would be of minor importance for the disappearance of H atom in the later stages of reaction. Further, any major contribution by reaction (5) would necessitate a large reduction in the final  $NH_3/N_2$  ratio from 2 which is observed experimentally.



As the decomposition proceeds, there is a possibility of secondary reaction occurring with the products. Reaction (7) could become important when the hydrogen concentration is sufficiently high to complete with reaction (3). Assuming<sup>23</sup>  $k_7 \sim 10^{12}$  cc./mole-sec. (an activation energy of 7 kcal./mole and a steric factor of  $10^{-2}$ ), it is estimated reaction (7) should become important only when the  $H_2/NH_2$  ratio approaches 20, and then only if the concentrations are sufficiently high to react during the time available.

Reactions (8) and (9) are possible chain steps involving hydrazine, Birse and Melville<sup>24</sup> determined the collision efficiency for the reaction of hydrogen atoms with hydrazine and assigned an activation energy of 7 kcal./mole and a steric factor of  $10^{-2}$  for reaction (8) and suggested (8b) as the dominant step. Using their values, the collision efficiency in our case at 2000°K. would be  $\sim 10^{-3}$  ( $k_8 \sim 10^{12}$  cc./mole-sec.), a value less than would be expected for the radical-radical reaction (5). A value of  $k_{8a} \sim 2 \times 10^{11}$  cc./mole-sec. is obtained by extrapolating the data of Schiavello and Volpi<sup>25</sup>. At the higher temperatures reaction (8) should make a minor contribution and should increase in possible importance at the lower temperatures. It is somewhat problematical whether or not reaction (8) could be important since a significance concentration of hydrogen atoms has not been established experimentally.

Reaction (9), the abstraction of hydrogen from hydrazine by amino radicals, is a likely reaction for the formation of any  $N_2H_3$ . The rate constant for this reaction has not been determined<sup>26</sup>, but should be of the same order as the reaction of hydrogen atoms with hydrazine. Assuming a comparable activation energy and steric factor, a collision efficiency of  $\sim 10^{-3}$  at 2000°K. is estimated ( $k_9 \sim 5 \times 10^{11}$  cc./mole-sec.). In order for this reaction to compete with reaction (3), the

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<sup>23</sup>Reference 21 was used as a guide in this estimation of  $k_7$ . This reaction is probably responsible for the formation of monodeuterated ammonia in the presence of excess deuterium.

<sup>24</sup>E. A. B. Birse and H. W. Melville, Proc. Roy. Soc. (London), A175, 164 (1940).

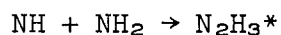
<sup>25</sup>M. Schiavello and G. G. Volpi, J. Chem. Phys., 37, 1510 (1962).

<sup>26</sup>However, a preliminary value of  $k_9 \sim 7.9 \times 10^{10}$  cc./mole-sec. has been determined at ambient temperature (E. J. Bair, private communication; M. H. Hanes, Ph.D. Thesis, Indiana University, 1962).

ratio of  $N_2H_4/NH_2$  needs to be of the order of 50, a value approached only at the lowest temperatures. It appears quite plausible from the above considerations and from the experimental results that the  $N_2H_3$  radical emerges as a significant intermediate at the lowest temperatures with a corresponding change to a chain mechanism.

Since nitrogen atoms were not observed, the disproportionation of NH with  $NH_2$  (or NH) should not be important.

An alternative reaction to (4) which may be considered for the reaction of NH radicals is:



followed by dissociation of the  $N_2H_3^*$  to give  $N_2H + H_2$ ,  $N_2 + H_2 + H$ , or  $N_2H_2 + H$ . If the activation energy for these dissociations are less than the energy of the newly formed nitrogen-nitrogen bond, then this reaction could be significant since  $(NH_2) > (NH)$ . On the basis of the estimated maximum concentration of  $N_2H$  or H, this reaction is probably not significant<sup>27</sup>. In any case, this would lower the value of  $k_3$  by only 1/3.

Although the proposed mechanism is not completely unequivocal, the very simple reaction scheme (1) through (4b) accounts for all of the experimental observations, within experimental error, except at the very low temperatures.

In principle  $k_{4a}$  can be evaluated on the basis of the proposed mechanism. At maximum NH concentration:

$$k_{4a} = \frac{k_3 (NH_2)^2}{2 (NH)^2}$$

In order to evaluate this expression it is necessary to evaluate the concentration of both NH and  $NH_2$  at the maximum NH, quantities which are not known experimentally. An estimate of  $k_{4b}$  can be made but at

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<sup>27</sup>See, however, footnote (22).

the risk of over-interpretation of the data. Assuming the NH maximum is not far removed in time from the NH<sub>2</sub> maximum and assuming all the mass 15 residue is NH, then an order of magnitude estimate of  $10^{14}$  cc./mole-sec. is obtained for  $k_{4a}$ <sup>28</sup>.

#### ACKNOWLEDGMENT

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<sup>28</sup>The NH formed in reaction (3) should be triplet NH since the singlet state is ~1.2 e.v. above the ground state (G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," 2nd Edition, D. VanNostrand Co., Inc., Princeton, N. J., 1950, p. 369.) Consideration of electron spin gives one in nine encounters in the singlet state of N<sub>2</sub>H<sub>2</sub>\* in reaction (4). This would suggest the value  $10^{14}$  cc./mole-sec. is too high since this value corresponds to about one in three collisions based on 3.3 Å for the collision cross section. A triplet state of N<sub>2</sub>H<sub>2</sub>\* below 110 kcal./mole (ref. 20) cannot, however, be completely excluded. Consideration of the uncertainties in  $k_3$ , along with the square of the uncertainties in the NH<sub>2</sub>/NH ratio (at maximum NH) makes this inconsistency somewhat academic at this point.

TABLE I

Observed First Order Rate Constants for the Disappearance  
of Hydrazine Diluted in Argon

<u>Reflected Shock Temp. °K.</u>	<u>Reflected Shock Press. Atm.</u>	<u>Mole % Hydrazine in Argon</u>	<u>k<sub>uni</sub> 10<sup>-9/2.3</sup> sec.<sup>-1</sup></u>
1400	0.146	1.0	1.3 <sup>a</sup>
1410	0.081	0.7	1.1
1420	0.081	1.0	1.1
1440	0.084	0.7	1.3
1460	0.079	0.7	1.5
1460	0.158	1.0	2.3
1480	0.160	1.0	2.8
1510	0.084	1.0	1.6
1520	0.129	0.7	2.9
1530	0.129	0.5	2.6
1530	0.166	1.0	3.8 <sup>b</sup>
1530	0.167	1.0	3.1 <sup>b</sup>
1540	0.080	0.6	2.2
1540	0.170	1.0	5
1550	0.089	1.0	2.3
1570	0.083	0.5	2.9
1660	0.138	0.5	6.5
1700	0.099	1.0	6.7 <sup>b</sup>
1730	0.051	0.5	4.0
1730	0.097	1.0	8.1
1740	0.054	0.7	4.0 <sup>b</sup>
1740	0.100	1.0	6.5
1740	0.105	1.0	6.1 <sup>b</sup>
1770	0.106	0.6	6.7
1770	0.206	1.0	12 <sup>b</sup>
1770	0.206	1.0	11 <sup>b</sup>
1820	0.055	0.6	5.5
1830	0.155	(0.3)	(9)
1850	0.040	1.0	5
1860	0.054	0.6	6.0 <sup>b</sup>

Table I (Contd.)

<u>Reflected Shock Temp. °K.</u>	<u>Reflected Shock Press. Atm.</u>	<u>Mole % Hydrazine in Argon</u>	<u><math>k_{uni} 10^{-3}/2.3</math> sec. <sup>-1</sup></u>
1870	0.110	0.7	10
1890	0.103	1.0	10
1890	0.124	(0.5)	(8)
1910	0.167	(0.1)	(10)
1970	0.062	0.7	6.7
2000	0.122	0.7	13
2000	0.178	(0.4)	(12)
2000	0.239	(0.5)	(18)
2060	0.130	0.5	13
2100	0.184	(0.1)	(15)
2180	0.171	0.5	8
2180	0.135	0.7	15
2190	0.135	0.5	15
2200	0.137	0.6	16
2200	0.275	0.7	28
2230	0.179	0.6	20
2230	0.279	0.7	28
2400	0.199	0.6	21
2440	0.152	0.6	18

<sup>a</sup>For many runs the 32 mass unit peak was recorded not only on the 35 mm. film but also on Polaroid film as a "gated output." When available the Polaroid record was used to determine these values because of the increased photographic accuracy.

<sup>b</sup>Analyzed by 50 volt electrons compared to 75 volt electrons normally used.

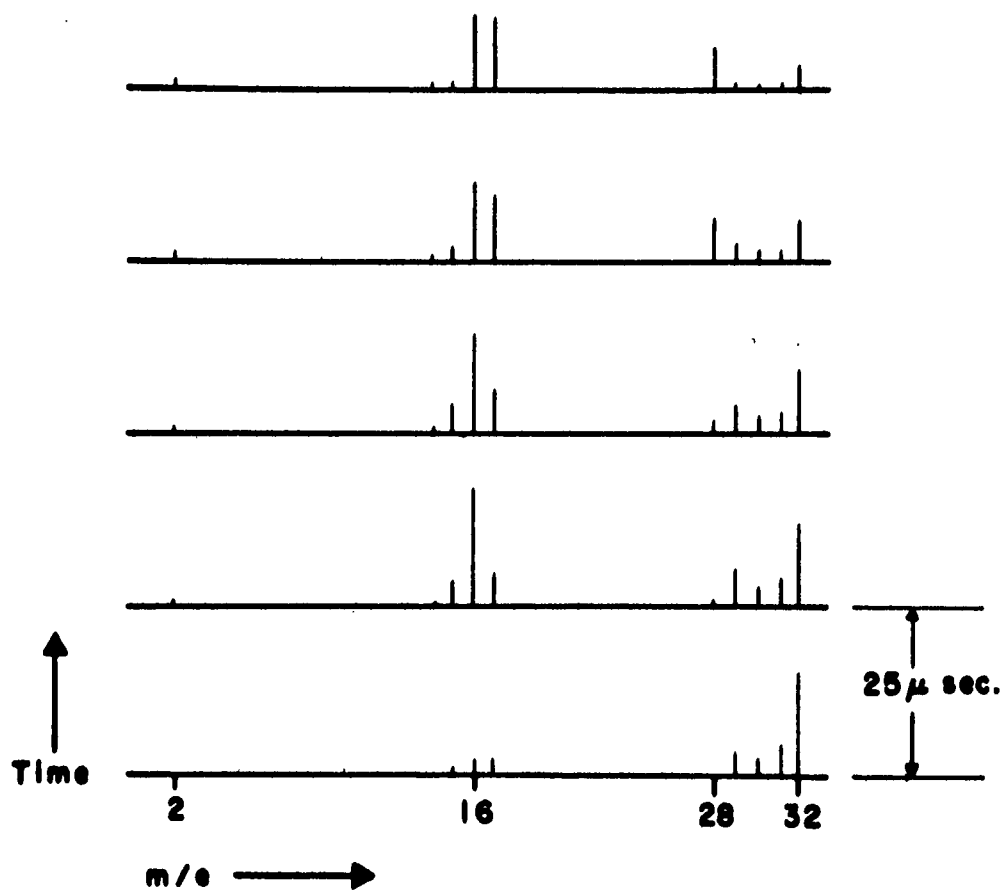


Figure 1 - Mass Spectral Bar Graph of the Experimental Record.  
Results for Hydrazine Decomposition at 1890°K. and  
0.12 Atm. (0.5% Hydrazine in Argon)  
Exclusive of the Argon Peaks.

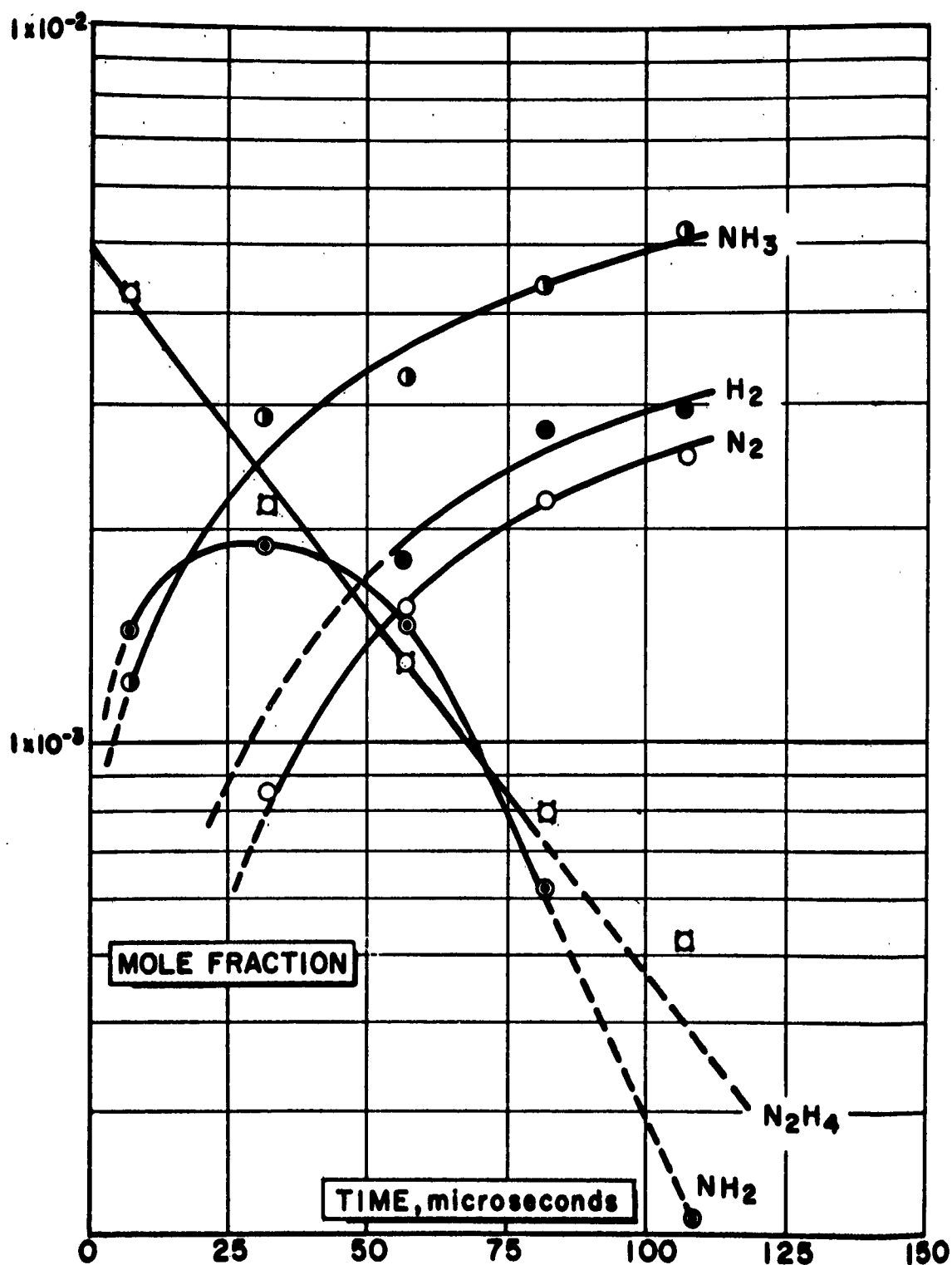


Figure 2 - Decomposition of  $N_2H_4$  at  $2060^\circ K$ . and  $0.13$  Atm.  
( $0.5\%$   $N_2H_4$  in Argon).

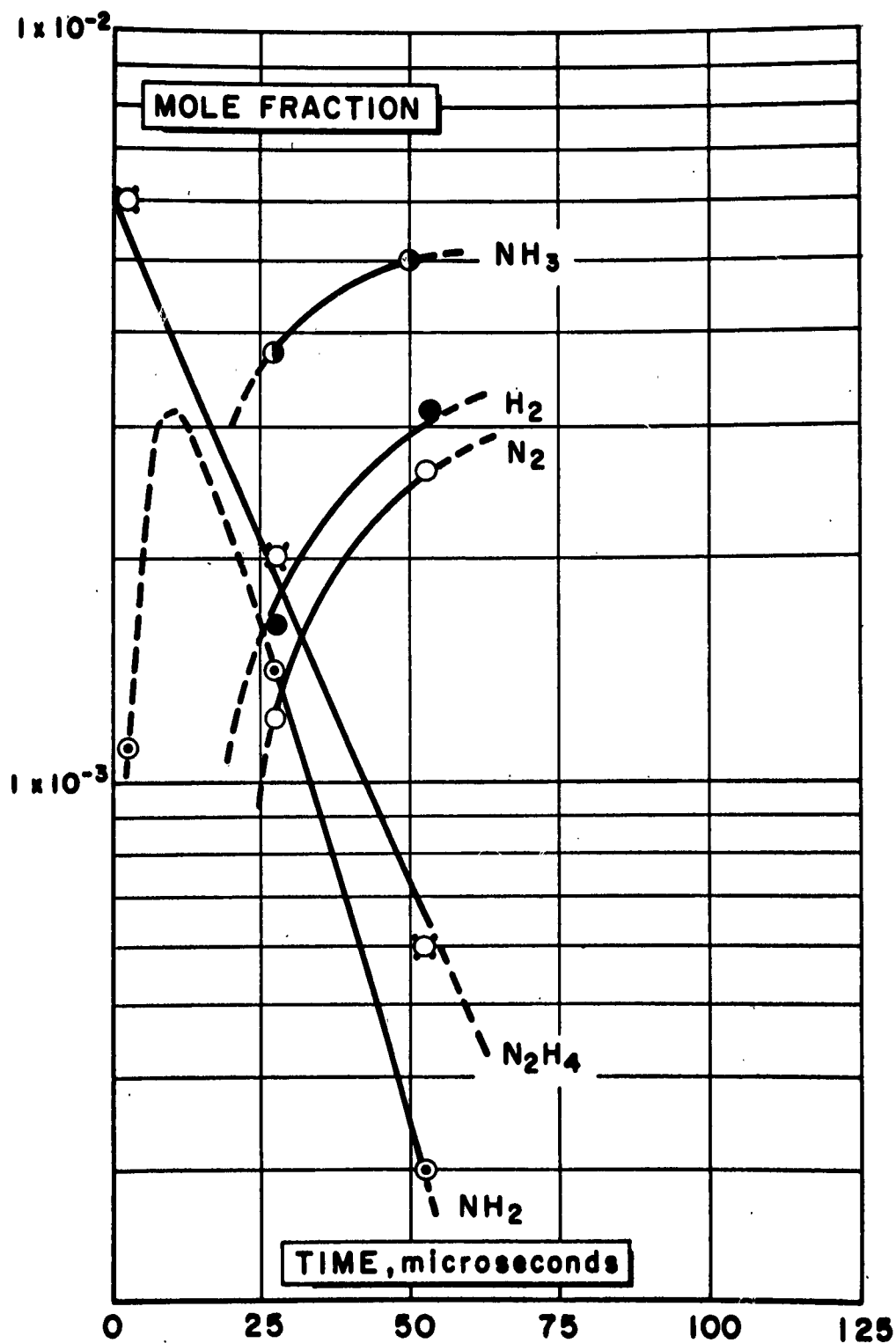


Figure 3 - Decomposition of  $N_2H_4$  at  $2440^\circ K.$  and  $0.15 \text{ Atm.}$   
( $0.6\% N_2H_4$  in Argon).



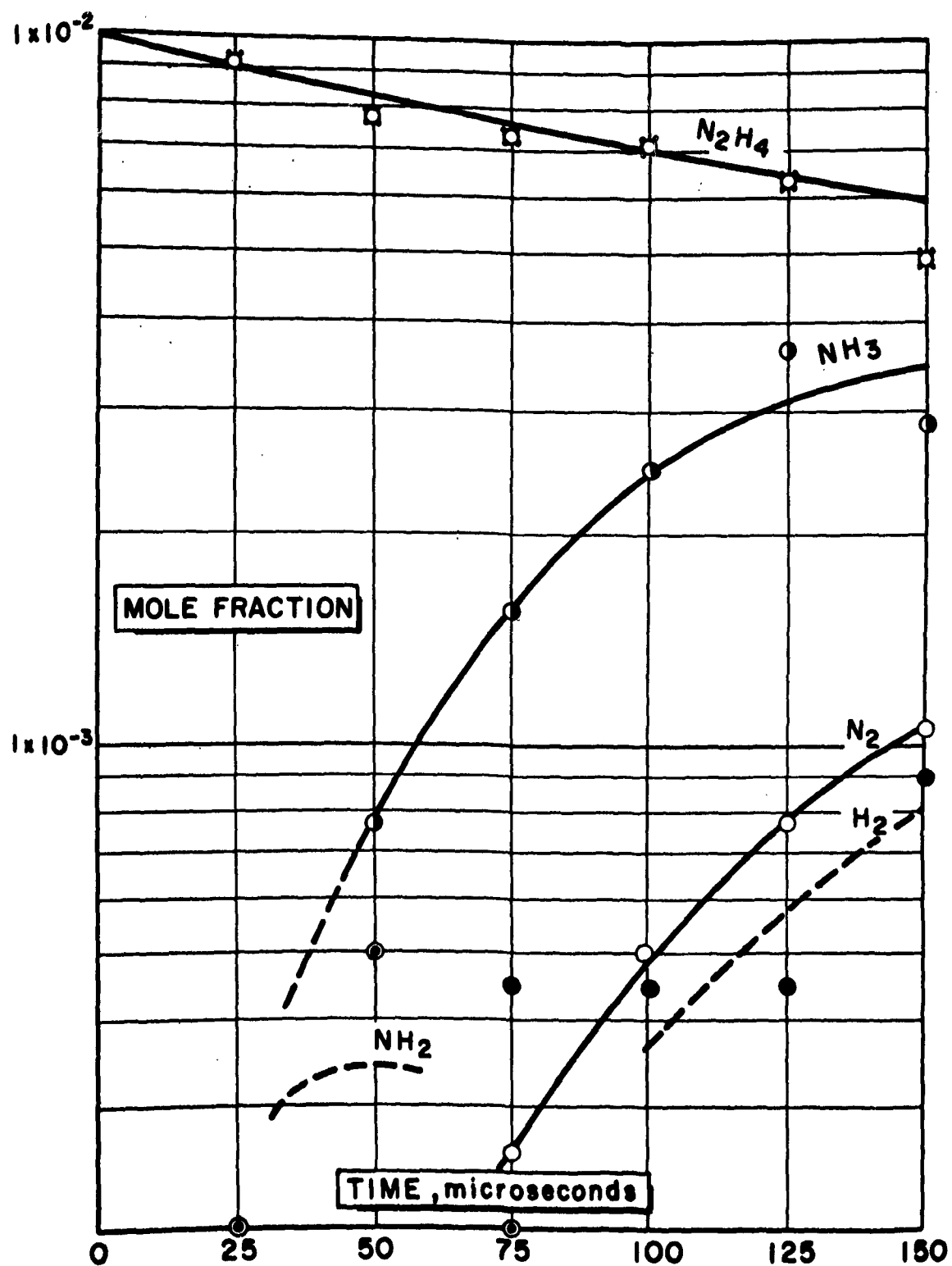


Figure 4 - Decomposition of  $N_2H_4$  at  $1510^\circ K.$  and  $0.083 \text{ Atm.}$  (1%  $N_2H_4$  in Argon).

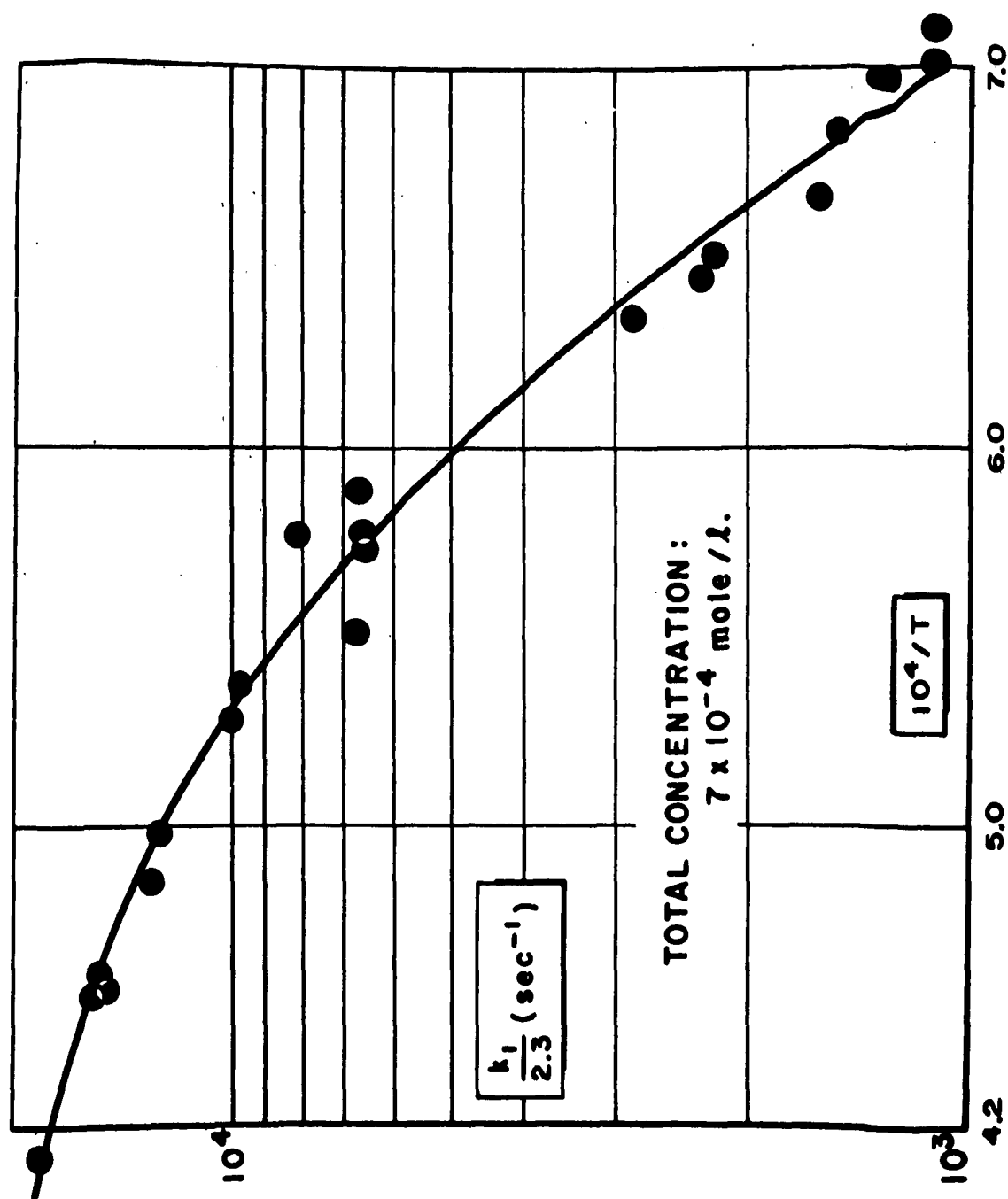


Figure 5 - Arrhenius Plot of the Observed First Order Rate Constants for the Decomposition of Hydrazine at Constant Total Concentration.